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14. ABSTRACT
Work has been completed in three areas of research. The first is in characterization of polyhedral oligomeric silsesquioxanes (POSS) and their attachment to backbones of organic-based oligomers. Using ion mobility, we have structurally characterized a wide variety of POSS species attaining good agreement with x-ray structures when available. We have also characterized di- and tri-siloxanes, POSS cages covalently bound via oxygen bridges. Most recently we have been able to insert a fluoride ion into the cage which should make detection of larger POSS/oligomer systems feasible. The second area of research deals with organic oligomeric systems. We have focused on systems with potential for opto-electronic or organo-electronic device formation. Successful work has been completed on a series of polyphenyl vinylenes and several paracyclophanes. Finally, we have generated and characterized the structures and ligand binding energies of both anionic and cationic gold and silver clusters (n = 2 to 13). These systems have been shown to have size-dependent catalytic behavior for double bond oxidation in small alkenes when dispersed on titanium oxide surfaces. We have focused on C2H4 and CH3CHCH2 due to their industrial importance.

15. SUBJECT TERMS

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Final Report

March 31, 2006

Structure and Energetics of Macromolecular Systems: POSS, Metal Clusters and Other Oligomeric Molecules

AFOSR Grant F49620-03-1-0046

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I. Progress has been made on the objectives listed below since the grant was initiated on January 1, 2003. Work that was discussed in previous reports (Sept. 1, 2003, Sept 1, 2004 and Sept. 1, 2005) will not be repeated here. In addition, a renewal proposal was submitted in February, 2005 that both summarized work completed and gave updated descriptions of work in progress. That work also will not be repeated here. Only new work initiated or completed since September 2005 will be discussed.

II. *Objectives*

A. Structure and Characterization of Polyhedral Oligomeric Silsesquioxanes (POSS)
B. Organic Oligomers
C. Metal Clusters: Structure and Ligand Energetics

III. *Progress and Accomplishments*

As noted above, there have been detailed annual reports filed giving progress up to September, 2005. Here we will briefly summarize work done between September 1 and December 31, 2005.

A. POSS

We have nearly completed studies on a series of R_7T_8-POSS monomers, in which fluoride ion is trapped in the POSS cage as demonstrated by both NMR chemical shifts and mass spectroscopy. These derivatives are prepared easily by reacting equi-molar amounts of the neutral POSS with tetramethylammonium fluoride in THF under rigorous anhydrous conditions. X-ray studies have shown that the F^- ion is situated in the center of the cage when R = phenyl and vinyl. The Edwards group has synthesized new well-characterized POSS systems with R = isobutyl, styryl, phenyl, trifluoropropyl, fluorohexyl, fluorooctyl, and fluorodecyl, in addition to these previously known phenyl and vinyl species. We have

negative ion ESI studies on all of these monomers and positive ion MALDI and ion mobility data (fluoride species cationized to R_7T_8-POSS (HF)·Na^+) were obtained for several of these species. Experimental cross-sections agree within 2% with x-ray structures and with modeled structures (see Tables 1 and 2).. Fluoride ion is also incorporated into cages in the presence of water, but side reactions occur which open cages and create a complicated series of oxo-anions. We have been able to determine many of these oxo-structures and model them. The fluoride monomer work is being written up for publication.

The momomer results are potentially very significant if the fluoride ion can be incorporated routinely into the POSS cage of oligomers. This simple derivatization would allow us to observe these systems and measure their cross sections. We have in hand a phenyl-POSS PMA 8-mer with one or two fluoride ions trapped in the POSS cages. We are in the process of characterizing it.

Table 1. Collision Cross-Sections (Å^2) of the POSS Fluoride Monomers.

Species	Mass	X-ray[a]	ESI (MALDI)	Theory
$[(CF_3(CF_2)_3(CH_2)_2]_8T_8F^-$			376	368
$Sty_8T_8F^-$		343	346	343
$Ph_8T_8F^-$	1051	260	268	260
$Vi_8T_8F^-$	651	168	165	167
$Vi_{10}T_{10}F^-$	809		189	190
$Vi_{12}T_{12}F^-$	967		210	212,214[c]
i-$Bu_7StyT_8F^-$	937			216
i-$Bu_6Sty_2T_8F^-$	985		258	257[d]
i-$Bu_5Sty_3T_8F^-$	1032		272	271[d]
i-$Bu_4Sty_4T_8F^-$	1076		282	284[d]
$(CF_3CH_2CH_2)_8T_8F^-$			251	256

Vi = vinyl; Ph = phenyl; Sty = styryl; i-Bu = i-butyl; $T_8 = Si_8O_{12}$

a. Structures obtained from Dr. Tim Haddad at ERC Inc., Air Force Research Laboratory

b. Calculated value for the neutral species.

c. Values correspond to two possible isomers.

d. Values identical for all possible isomers within experimental error.

Table 2. Collision Cross-Sections (Å^2) of the Sodiated POSS Fluoride Monomers.

Species	X-ray	MALDI (Na^+)	Theory (Na^+)
$Na^+Sty_8T_8$ ·HF		321	325
$Na^+Ph_8T_8$·HF	263[b]	254	257
$Na^+Vi_8T_8$·HF	168[b]	165	167

Vi = vinyl; Ph = phenyl; Sty = styryl; i-Bu = i-butyl; $T_8 = Si_8O_{12}$

a. Structures obtained from Dr. Tim Haddad at ERC Inc., Air Force Research Laboratory

b. Calculated value for the neutral species.

B. Metal Clusters

The work on gold clusters has now been completed and a manuscript is in draft form.

IV. Papers published or in press

1. Conformation and Luminescence of Isolated Molecular Semiconductor Molecules, M. A. Summers, P. R. Kemper, J. E. Bushnell, M. R. Robinson, G. C. Bazan, M. T. Bowers, and S. K. Buratto, *J. Am. Chem. Soc.* **125**, 5199 (2003).

2. Gas Phase Conformations: The Ion Mobility/Ion Chromatography Method, T. Wyttenbach and M. T. Bowers, Topics in Current Chemistry, Vol. 225: Modern Mass Spectrometry, edited by C. A. Schalley (Springer, Berlin, pp. 207-232) (2003).

3. 3-Dimensional Structural Characterization of Cationized Polyhedral Oligomeric Silsesquioxanes (POSS) with Styryl and Phenylethyl Capping Agents, E. S. Baker, J. Gidden, D. P. Fee, P. R. Kemper, S. E. Anderson, and M. T. Bowers, *Int. J. Mass Spectrom.*, Special Issue Honoring Rob Dunbar, **227**, 205 (2003).

4. Bonding Interactions in $Ag^+(O_2)_n$ and $Ag_2^+(O_2)_n$ Clusters: Experiment and Theory, M. J. Manard, P. R. Kemper, and M. T. Bowers, *Int. J. Mass Spectrom.,* Special Issue Honoring Helmut Schwarz, **228**, 865 (2003).

5. Isomeric Structural Characterization of Polyhedral Oligomeric Silsesquioxanes (POSS) with Styryl and Epoxy Phenyl Capping Agents, E. S. Baker, J. Gidden, S. E. Anderson, T. S. Haddad, and M. T. Bowers, *Nano Letters* **4,** 779 (2004).

6. Diastereomer Assignment of an Olefin-Linked Bis-paracyclophane by Ion Mobility Mass Spectrometry, E. S. Baker, J. W. Hong, J. Gidden, G. P. Bartholomew, G. C. Bazan, and M. T. Bowers, *J. Am. Chem. Soc.* **126**, 6255 (2004).

7. The Determination of Cis-Trans Conformations in Tetrahedral p-Phenylene Vinylene Oligomers, J. E. Bushnell, P. R. Kemper, G. C. Bazan, and M. T. Bowers, *J. Phys. Chem. A* **108**, 7730 (2004).

8. Sequence Dependent Conformations of Glycidal Methacrylate/Butyl Methacrolate Copolymers in the Gas Phase, E. S. Baker, J. Gidden, W. J. Simonsick, M. C. Grady, and M. T. Bowers, *Int. J. Mass Spectrom.*, Special Issue on Polymers, **238**, 279 (2004).

9. Microstructural and Conformational Studies of Polyether Copolymers, A. T. Jackson, J. H. Scrivens, J. P. Williams, E. S. Baker, J. Gidden, and M. T. Bowers, *Int. J. Mass Spectrom.* **238**, 287 (2004).

10. Dissociation Reactions of Diatomic Silver Cations with Small Alkenes: Experiment and Theory, M. J. Manard, P. R. Kemper, C. J. Carpenter, and M. T. Bowers, *Int. J. Mass Spectrom.* **241**, 99 (2005).

11. Binding Interactions of Mono- and Diatomic Silver Cations with Small Alkenes: Experiment and Theory, M. J. Manard, P. R. Kemper, and M. T. Bowers, *Int. J. Mass Spectrom.* **241**, 109 (2005).

12. Structure of Hybrid Polyhedral Oligomeric Silsesquioxane Propyl Methacrylate Oligomers Using Ion Mobility Mass Spectrometry and Molecular Mechanics S. E. Anderson, E. S. Baker, C. Mitchell, T. S. Haddad, and M. T. Bowers, *Chem. Mater.* **17**, 2537 (2005).

13. Probing the Structure of Gas-Phase Metallic Clusters via Ligation Energetics: Sequential Addition of C_2H_4 to Ag_m^+ (m = 3-7), M. J. Manard, P. R. Kemper, and M. T. Bowers, *J. Am. Chem. Soc.* **127**, 9994 (2005).

V. Personnel Supported

A. Senior	B. Junior
Dr. Paul Kemper	Mr. Manuel Manard
Dr. Thomas Wyttenbach	Ms. Erin Baker
Dr. Jennifer Gidden	Mr. John Bushnell
Dr. Stan Anderson	Ms. Dena Bodzin
	Ms. Connie Mitchell

VI. Papers Presented

A. Invited Lectures at Meetings

1. Field and Franklin Award Symposium, American Chemical Society Meeting, New Orleans, LA, Mar. 2003

2. Air Force Contractors Meeting, San Diego, CA, May 2003

3. Lecturer, Gordon Conference on Biological Molecules in the Gas Phase, New London, CT, Jul. 2003

4. Keynote Lecture, Triennial International Conference on Mass Spectrometry, Edinburgh, Scotland, Aug. 30 - Sep. 4, 2003

5. International Symposium on Clusters and Nano-Assemblies: Physical and Biological Systems, Richmond, VA, Nov. 2003

6. Plenary Lecture, Department of Energy Basic Energy Sciences Analysis Program Contractors Meeting, Annapolis, MD, Feb. 2004

7. Plenary Lecture, German Mass Spectrometry Meeting, Leipzig, Germany, Mar. 2004

8. Euresco Conference on Molecules of Biological Interest in the Gas Phase, Exeter, UK, Apr. 2004

9. Keynote Lecture, American Society for Mass Spectrometry, From Solution to the Gas Phase, May, 2004

10. Distinguished Contribution Award Lecture, American Society for Mass Spectrometry, Nashville, TN, May 2004

11. JANNAF 32nd Propellant and Explosives Development and Characterization Meeting, Seattle, WA, Jul. 2004

12. Plenary Lecture, Italian Mass Spectrometry Society, Bari , Italy, Sept. 2004

13. Plenary Lecture, Australian and New Zealand Society for Mass Spectrometry, Adelaide, Australia, Jan. 2005 (declined due to injury)

14. Lecturer, Gordon Conference on Structures, Energetics and Reactions of Gas Phase Ions, Ventura, CA, Feb. 2005

15. Air Force Contractors Meeting, Monterey, CA, May 2005

B. Contributed Papers at Meetings

1. Five Papers, Ion Chemistry Conference, Lake Arrowhead, CA, Jan. 2003

2. American Society of Mass Spectrometry, Montreal, Canada, Jun. 2003

3. Four Papers, Ion Chemistry Conference, Lake Arrowhead, CA, Jan. 2004

4. Four Papers, Ion Chemistry Conference, Lake Arrowhead, CA, Jan. 2005

C. Seminars at Universities

1. UC San Diego, Jan. 2003

2. UC Santa Barbara, Apr. 2003

3. Univ. Colorado, Boulder, Nov 2004

4. Cal. Tech., Nov 2004

VII. Honors/Awards

New

none

Continuing/Prior

1. Honoree of a Special Issue of the International Journal of Mass Spectrometry (There were 84 papers comprising all of vols. 185, 186 and 187 -- June 1999)

2. Fellow, American Physical Society (elected 1987)

3. Fellow, American Association for the Advancement of Science (elected 1994)

4. Fellow, John Simon Guggenheim Foundation (1995 Calendar Year)

5. Nobel Laureate Signature Award, American Chemical Society (1989)

6. Faculty Research Lecturer, University of California at Santa Barbara (1994) (This is the highest award given by the UCSB Academic Senate. There is one award given each year campus-wide.)

7. Frank H. Field and Joe. L Franklin Award for Outstanding Achievement in Mass Spectrometry, American Chemical Society (1996)

8. Thomson Gold Medal, International Mass Spectrometry Society (1997) (This is the highest award given internationally in mass spectrometry. There is one award given each year.)

9. Distinguished Contribution Award, American Society of Mass Spectrometry (2004) (This is the highest award presented by ASMS. It is given to one person each year for a specific scientific contribution.)

10. Honoree of a Special Issue of the Journal of the American Society of Mass Spectrometry (Volume 16, Issue 7) in recognition of the Distinguished Contribution Award presented by the Society May 2004

VIII. Transitions

None in this time period

IX. New Discoveries, Innovations or Patent Disclosures

None